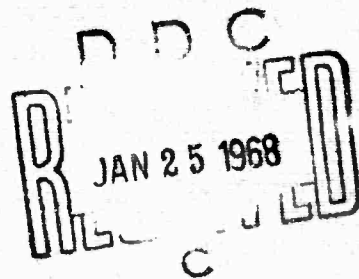54

Measurement of Atomic Kinetics of Solidification Using Peltier Heating and Cooling

R. J. SCHAEFER AND M. E. GLICKSMAN

Metal Physics Branch
Metallurgy Division

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Washington, D.C.

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ABSTRACT

Periodic Peltier heating and cooling may be generated at a solid/ liquid interface by the passage of an alternating electric current. Melting and freezing will then occur at rates which will be influenced by the kinetic law of molecular attachment relating solidification velocity to interface temperature. The equation describing the interface attachment kinetics may be determined by measuring the response of a solid/ liquid interface to square-wave Peltier heating and cooling. The mathematical methods required for extracting the kinetic equation by analysis of the waveform of interface motion show that this technique should give distinguishably different waveforms for linear, parabolic, and exponential kinetics. There are advantages of the method, but precautions must be taken to eliminate possible confusing effects.

PROBLEM STATUS

This is a final report on one phase of the problem; work on other phases is continuing.

AUTHORIZATION

MEASUREMENT OF ATOMIC KINETICS OF SOLIDIFICATION
USING PELTIER HEATING AND COOLING

INTRODUCTION

At present, little conclusive information is available concerning the atomic mechanisms by which metal crystals grow from their melts. Observations of morphological features, such as crystallographic facets, have usually been of a qualitative nature. An experimental measurement of the relation between crystal growth velocity and the supercooling at the solid/liquid interface would be extremely informative, because the mathematical form of this relation has been predicted theoretically on the basis of several proposed crystal growth mechanisms. The present report describes a quantitative method which can be used to investigate this relation in metals and semiconductors.

Three important kinetic relationships have been predicted on the basis of three distinct atomic crystallization processes. For continuous growth at atomically rough interfaces, where all surface sites are equivalent, the interface velocity is expected to be a linear function of the interface supercooling (1) and may be written

$$v = \mu_1 \theta , \tag{1}$$

where θ represents the temperature deviation of the interface from the equilibrium temperature, and μ_1 is the linear kinetic coefficient. When atoms are added to the crystal at surface steps generated by dislocations, the predicted kinetic relation (2) has the form

$$v = \mu_2 \theta |\theta| . \tag{2}$$

If the crystal grows by the independent nucleation of successive layers on an atomically smooth (singular) surface, an exponential kinetic relation (3) is obtained;

$$v = \mu_3 \frac{\theta}{|\theta|} e^{-\mu_4 / |\theta|} . \tag{3}$$

The absolute-value signs in Eqs. (2) and (3) have been introduced to make the v's odd functions of the θ's, on the assumption that freezing and melting kinetics are the same. While the measurement of an experimental relation between v and θ would, in principle, enable one to distinguish between the mechanisms leading to Eqs. (1) through (3), in practice great difficulty is encountered in the measurement of θ. In metals substantial growth velocities are expected even at small values of θ, but such rapid growth almost invariably results in complex, nonplanar interfaces with large temperature gradients associated with the release of the latent heat of fusion. In such situations the temperature of the interface cannot be measured with sufficient accuracy in any known direct fashion.

A few years ago Kramer and Tiller (4) proposed an experiment in which interface velocities and temperature variations could be calculated from measurements of the attenuation of a thermal wave propagated through a solid/liquid interface. The great sensitivity in that experiment was made possible by the measurement of periodic variations of temperature about the equilibrium temperature, rather than of absolute instantaneous or steady-state temperatures. While the Kramer-Tiller thermal-wave experiment has

been used to investigate the solidification of tin (5,6) and ice (7), the correctness of the execution and interpretation of that experiment has been questioned (8-10). Some of the more serious experimental problems have been the prevention of convection in the liquid and the elimination of "short circuit" paths by which the thermal waves flow along the container walls instead of through the solid/liquid interface. Also, the mathematical treatment of situations in which the kinetic relation between interface supercooling and crystallization velocity is nonlinear has been very difficult (11). Finally, published data on tin, derived from that experiment, have been conflicting and inconclusive (5,6,8-10).

We now describe a new experiment which has similarities to the method of Kramer and Tiller but which eliminates some of the experimental and analytical difficulties of their approach.

DESCRIPTION OF EXPERIMENT

Our experiment derives kinetic data from an analysis of the response of a solid/liquid interface to a periodic input of heat directly at the interface; this heat input is introduced using Peltier (thermoelectric) heating and cooling generated by an alternating electric current passing through the interface. The resulting interface motion is measured and the corresponding interface temperature variation calculated, almost the reverse of the procedure described by Kramer and Tiller, who measured temperature variations and then calculated velocities.

To understand the response of a solid/liquid interface to Peltier heating, first consider a system solidifying with infinite kinetics, so μ_1 in Eq. (1) is infinite, and θ is always zero. When a direct current of density j_0 amp/cm^2 passes through this interface, Peltier heat is emitted or absorbed, depending on the direction of current flow, in the amount $q_P = Pj_0$ per unit interface area. Here P is the Peltier coefficient between solid and liquid. Since the assumption of infinite kinetics demands that the interface remain at the equilibrium temperature, latent heat must be generated to cancel the Peltier heat exactly. Thus, the interface must move with a velocity $v_0 = Pj_0/\lambda\gamma$, where λ is the latent heat of fusion in joules per gram, and γ is the mass density. If a square-wave electric current, constant in magnitude but alternating in direction, passes through the solid/liquid interface, the alternate (Peltier) heating and cooling will result in a "sawtooth" motion of the interface, as alternate melting and freezing occur with velocity $\pm v_0$. Joule heating, which is independent of current direction, will remain essentially constant with time for a symmetrical square wave and, thus, will not affect the periodic motion of the solid/liquid interface. A small periodic variation in Joule heating, due to the change of electrical resistance as the interface moves, is shown in a later section to be negligible compared to the periodic variation in Peltier heating.

When interface kinetics are not infinitely rapid, the periodic motion of the interface must be associated with periodic changes in interface temperature. These changes in interface temperature imply that a temperature wave is propagated into the solid and liquid material on either side of the interface and that the latent heat does not exactly cancel the Peltier heat. Under these conditions, the "sawtooth" motion of the solid/liquid interface becomes distorted, and if this distorted waveform can be measured, then the periodic variation of the solid/liquid interface temperature can be calculated.

For the experimental measurement of the response of a solid/liquid interface to square-wave Peltier heating, the material to be investigated is enclosed in a cylindrical container equipped with four electrodes (Fig. 1). This container is positioned in a temperature gradient so that the lower part of the material is solid and the remainder is liquid, with the solid/liquid interface lying between the second and third electrodes. The first and fourth electrodes introduce the square-wave electric current which generates Peltier heating and cooling, thus causing the periodic motion of the solid/liquid interface.

Fig. 1 - Apparatus for determination of solidifi-
cation kinetics, showing solid/liquid interface,
current electrodes (1 and 4), and potential elec-
trodes (2 and 3)
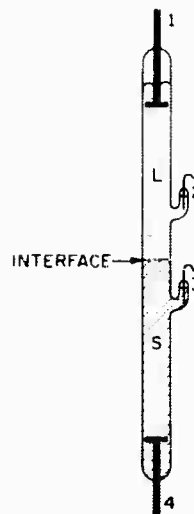
Since solid and liquid metal have different electrical resistivities, motions of the inter-
face cause changes in the resistance of the metal column between electrodes 2 and 3; the
interface motions are detected by monitoring these resistance changes.

Considerations of Joule heating, radial heat flow, and sensitivity of measurement,
indicate that the optimum diameter of the metal specimen is about 1 mm, and the corre-
sponding amplitude of the square-wave current is in the range of 2 to 5 amp. Also, it is
estimated that the appropriate fundamental frequency for the square-wave current induc-
ing the interface motion should be roughly 10 Hz. For the measurement of resistance
variations due to interface motions, a high-frequency (100 kHz) sine-wave current ap-
proximately 1 amp in amplitude is superimposed on the square wave. Because the re-
sistance variations due to interface motion are small, it is essential that a bridge method
be used for this measurement. Complete details of the electrical circuitry involved will
be presented in a later experimental report.

Experiments of the type under consideration are applicable only to substances with
sufficient electrical conductivity to allow introduction of the current causing the Peltier
heating and cooling. In addition, the solid and liquid must differ in electrical conductiv-
ity by some amount sufficient to permit accurate resistometric determinations of inter-
face motions. Finally, the Peltier coefficient at the solid/liquid interface must be large
enough to produce adequate rates of heating and cooling. Bismuth and germanium show
promising combinations of these properties, and several other elements with relatively
low melting temperatures, such as mercury, gallium, and tin, also appear to be suitable.

ANALYSIS OF HEAT FLOW

We will now show how interface temperature variations can be calculated from meas-
ured waveforms of interface motion. We shall start the heat-flow analysis with a consid-
eration of the situation in which an interface between two semi-infinite substances lies
along the plane $x = 0$, with substance 1 occupying the space $x > 0$ and substance 2 occupy-
ing the space $x < 0$. One-dimensional heat flow will be assumed throughout the analysis.
Let heat from some sinusoidal source with angular frequency $n\omega_0$ be emitted from this
interface at a rate of $q_n = |q_n| \sin(n\omega_0 t)$ per unit area. The temperature variations re-
sulting in each substance from this heating will be given by solutions of the heat-flow
equation

$$\frac{\partial^2 \Theta_{jn}}{\partial x^2} - \frac{1}{\alpha_j} \frac{\partial \Theta_{jn}}{\partial t} = 0 , \qquad j = \begin{cases} 1, & x > 0 \\ 2, & x < 0 \end{cases} , \qquad (4)$$

with the boundary condition

$$|q_n| \sin(n\omega_0 t) = -k_1 \left.\frac{\partial \Theta_{1n}}{\partial x}\right|_{x=0} + k_2 \left.\frac{\partial \Theta_{2n}}{\partial x}\right|_{x=0} \qquad (5)$$

expressing the fact that no heat can accumulate at the interface. The upper case Θ is used to express temperature as a function of x, with the lower case θ always indicating temperature at the interface ($x = 0$) only. Here the α's and k's represent the thermal diffusivities and conductivities, respectively, of the two phases. The solutions of these equations are readily obtained, for example, by an extension of the solution given by Jakob (12) and may be written

$$\Theta_{1n} = \frac{A}{\sqrt{(n\omega_0)}} e^{-\sqrt{(n\omega_0/2\alpha_1)}\,x} |q_n| \sin\left[n\omega_0 t - \sqrt{(n\omega_0/2\alpha_1)}\,x - \pi/4\right] \qquad (6a)$$

and

$$\Theta_{2n} = \frac{A}{\sqrt{(n\omega_0)}} e^{+\sqrt{(n\omega_0/2\alpha_2)}\,x} |q_n| \sin\left[n\omega_0 t + \sqrt{(n\omega_0/2\alpha_2)}\,x - \pi/4\right] . \qquad (6b)$$

where $A = [\sqrt{\alpha_1 \alpha_2}/(k_1 \sqrt{\alpha_2} + k_2 \sqrt{\alpha_1})]$. Figure 2 illustrates the form of these functions at several stages during the cycle for a wave of frequency 100 Hz diffusing from a boundary between solid and liquid bismuth. It is seen that the damping is extremely rapid, with the oscillations propagating only about one wavelength into either medium before becoming negligibly small compared to the interface temperature variations.
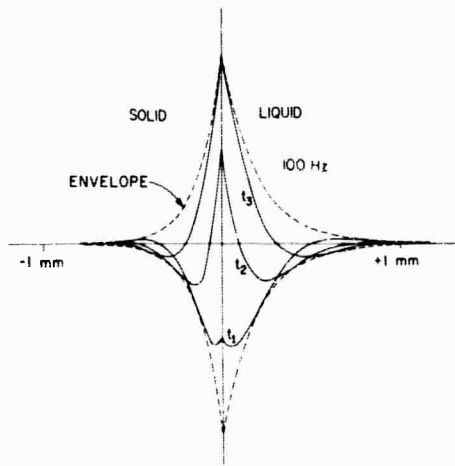

Fig. 2 - Thermal wave, frequency 100 Hz, propagating from interface between solid and liquid bismuth. The wave is shown at three stages: t_1, $t_2 = t_1 + \pi/3\omega$, and $t_3 = t_1 + 2\pi/3\omega$. Dashed lines show envelopes of the damped sine waves.

The expression for the interface temperature variation θ_n can be obtained by setting $x = 0$ in Eqs. (6). Hence,

$$\theta_n = \frac{A}{\sqrt{(n\omega_0)}} |q_n| e^{i(n\omega_0 t - \pi/4)} = \frac{A}{\sqrt{(n\omega_0)}} q_n e^{-i\pi/4} , \qquad (7)$$

where we have used a complex notation for the sine function and written q_n for the sinusoidally varying $|q_n|e^{in\omega_0 t}$. Where the complex notation is used, it is to be understood that the actual values of the functions represented are given by the imaginary part of the complex functions.

The total periodic heat emission from the solid/liquid interface is, in fact, the algebraic sum of the Peltier and latent heat emissions and may be expressed as the sum of sinusoidal components, so we may write

$$q(t) = \sum_n |q_n| e^{i(n\omega_0 t + \phi_n)} = q_P(t) + q_\ell(t) = q_P(t) + \lambda\gamma v(t) . \tag{8}$$

Since $q_P(t)$ is known from the square-wave electric current and $q_\ell(t)$ may be determined by measuring $v(t)$, we can find the sets of $|q_n|$ and ϕ_n which describe the total interface heat emission. The corresponding total interface temperature variations are then calculated from Eq. (7) as

$$\theta(t) = \frac{A}{\sqrt{\omega_0}} \sum_n |q_n| \frac{e^{i(n\omega_0 t + \phi_n - \pi/4)}}{\sqrt{n}} . \tag{9}$$

The calculated $\theta(t)$ is finally plotted against the measured $v(t)$ to reveal the experimental kinetic relation.

It may be pointed out here that this experiment uses an analysis of waveform, whereas the Kramer-Tiller experiment employs measurements of the amplitude of the transmitted thermal waves. Those authors point out that a waveform analysis could in principle be used to derive the kinetic relation from their experiment, but that the possibility for error in such an analysis is large. The present experiment would measure waveforms directly at the interface, rather than measuring them after their content of higher harmonics has been reduced by conducting through some length of material. Thus, waveform measurements are expected to be more accurate in the present experiment, and the analysis in terms of waveform more straightforward.

EXPECTED WAVEFORMS

It is desirable to have quantitative a priori knowledge of the waveforms of interface motion which would result from behavior described by the kinetic relations (1) through (3). These waveforms can be generated by either a Fourier-analysis method (for linear kinetics) or an integral-equation method (for any kinetic law).

To solve the case of linear kinetics, we first note that each frequency component of the total interface temperature variation is the sum of Peltier and latent heat contributions

$$\theta_n = \theta_{Pn} + \theta_{\ell n} . \tag{10}$$

When the kinetics are linear, we can express the latent heat emission by the interface as $q_{\ell n} = -\lambda\gamma v_n = -\lambda\gamma\mu_1\theta_n$. If we now consider a sinusoidal interface motion due to a sinusoidal input of Peltier heat at the interface with frequency $n\omega_0$, we have, from Eq. (7),

$$\theta_{\ell n} = \frac{A}{\sqrt{n\omega_0}} q_{\ell n} e^{-i\pi/4} = -\frac{B}{\sqrt{n}} \theta_n e^{-i\pi/4} , \tag{11}$$

where we have used $B = A\lambda\gamma\mu_1/\sqrt{\omega_0}$. Substituting Eq. (11) into Eq. (10), we can solve for θ_n as a function of θ_{Pn}, obtaining

$$\theta_n = -\frac{\theta_{Pn}}{1 + (B^4/n^2)} \left(1 - \frac{B}{\sqrt{n}} e^{-i\pi/4} + \frac{B^2}{n} e^{-2i\pi/4} - \frac{B^3}{\sqrt{n^3}} e^{-3i\pi/4}\right). \tag{12}$$

T.is expression rel:tes the total interface temperature variation to the tempe.ature variation due to Peltier heat alone; the interface velocity is then given by Eq. (1). This velocity may be related to the original sinus.idal input of Peltier heat by expressing θ_{Pn} in Eq. (12) in terms of q_{Pn} by the use of Eq. (7).

For the square-wave current input of amplitude j_0 amp/cm^2 and angular fundamental frequency ω_0, we can express the Peltier heating as $q_P = \Sigma q_{Pn}$, with

$$q_{Pn} = \frac{4Pj_0}{\pi} \frac{e^{in\omega_0 t}}{n} \, , \quad n \text{ odd}. \tag{13}$$

The interface temperature variation can be written $\theta = \Sigma\theta_n$, with the θ_n values given by Eq. (12).

Equation (7) may be used to express the θ_{Pn} values of Eq. (12) in terms of the q_{Pn} values of Eq. (13). The resulting expression for θ may be normalized by multiplying by the kinetic coefficient μ_1 to give the velocity, and dividing by the velocity for infinite kinetics v_0. The normalized velocity $\Psi(\omega_0 t)$ may be written

$$\Psi(\omega_0 t) = \frac{v}{v_0} = \frac{4}{\pi} B \sum_n \frac{\sqrt{n}}{n^2 + B^4} \left[\sin(n\omega_0 t - \pi/4) - \frac{B}{\sqrt{n}} \sin(n\omega_0 t - 2\pi/4) \right.$$

$$\left. + \frac{B^2}{n} \sin(n\omega_0 t - 3\pi/4) - \frac{B^3}{\sqrt{n^3}} \sin(n\omega_0 t - \pi) \right]. \tag{14}$$

Computer-generated curves of this function are shown in Fig. 3 for various values of B; for $B < 10$, values of n up to 199 were used, while for $B = 10$, values up to 999 were used. Also shown are the computer-generated time integrals of this function, giving the displacement of the interface as a fraction of the total amplitude the oscillati·ns would have with infinite kinetics.

The analysis given above is not readily extend·d to cases of nonlinear kinetics. However, an alternative method employing an integral equation may be used, if we make the additional assumption that the interface velocity comes close to the steady-state velocity before each periodic reversal of current direction.

In this method we consider first an interface between two semi-infinite media initially at uniform temperature $\Theta = \theta_0$. Suppose that at time $t = t'$ this interface emits a small pulse of heat of magnitude δq. The temperature distribution in the two media at times $t > t'$, due to the pulse of heat at time $t = t'$, will then be given by

$$\Theta_j = \theta_0 + \delta\Theta_j = \theta_0 + \delta q \frac{A}{\sqrt{\pi}} \frac{e^{-x^2/4a_j(t-t')}}{\sqrt{(t-t')}} \, , \quad j = \begin{cases} 1, & x > 0 \\ 2, & x < 0 \end{cases}. \tag{15}$$

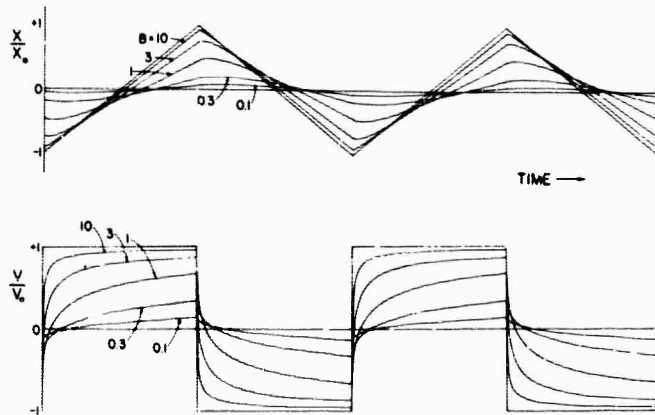where A has the same value as in Eqs. (6).

Fig. 3 - Interface displacement and velocity
waveforms, generated from Eq. (14) for in-
terfaces with linear kinetics. The curves have
been normalized by dividing by the displace-
ment and velocity of an interface with infinite
kinetics.

The interface temperature is given by setting $x = 0$ in Eq. (15):

$$\theta = \theta_0 + \delta\theta = \theta_0 + \delta q \frac{A}{\sqrt{\pi}} (t - t')^{-1/2} . \tag{16}$$

If, instead of emitting a single pulse of heat, the interface emitted heat continuously at a
rate of $q(t')$, starting at $t' = 0$, we can write $\delta q = q(t') dt'$, and the total temperature
at the interface will be given by

$$\theta = \theta_0 + \frac{A}{\sqrt{\pi}} \int_{t'=0}^{t} \frac{q(t')}{\sqrt{(t-t')}} dt' . \tag{17}$$

If now an interface is initially moving at its steady-state velocity under the influence
of a direct current, the Peltier heat is canceled by the latent heat and no net heat is
emitted by the interface; the temperature in both media is then uniform at $\overline{\theta_0}$. If the
current is reversed at time $t = 0$, the function $q(t')$ in Eq. (17) will be composed of two
terms, due to Peltier and latent heat, now no longer canceling:

$$q(t') = Pj_0 - \lambda \gamma v [\theta(t')] . \tag{18}$$

Substituting into Eq. (17) and performing the integration on the first term, we obtain

$$\theta(t) = \theta_0 + \frac{A}{\sqrt{\pi}} \left\{ 2Pj_0 \sqrt{t} - \lambda \gamma \int_{t'=0}^{t} \frac{v[\theta(t')]}{\sqrt{(t-t')}} dt' \right\} . \tag{19}$$

Substituting the kinetic relations (1) through (3) into this expression yields

$$\Psi(\omega_0 t) = 1 - \frac{B}{\sqrt{\pi}} \left\{ 2 \sqrt{(\omega_0 t)} + \int_{\omega_0 t'=0}^{\omega_0 t} \frac{\Psi(\omega_0 t') d(\omega_0 t')}{\sqrt{(\omega_0 t' - \omega_0 t)}} \right\} . \tag{20a}$$

$$\theta(t) = \theta_0 + \frac{A}{\sqrt{\pi}} Pj_0 \left\{ 2\sqrt{t} - \frac{1}{\theta_0^2} \int_{t'=0}^{t} \frac{\theta(t')|\theta(t')|dt'}{\sqrt{(t-t')}} \right\}. \tag{20b}$$

and

$$\theta(t) = \theta_0 + \frac{A}{\sqrt{\pi}} Pj_0 \left\{ 2\sqrt{t} - e^{+\mu_4/|\theta_0|} \int_{t'=0}^{t} \frac{\theta(t')e^{-\mu_4/|\theta(t')|}dt'}{|\theta(t')|\sqrt{(t-t')}} \right\}. \tag{20c}$$

where Eq. (20a) has been normalized the same way Eq. (14) was; similar normalizations are not useful for the nonlinear kinetic laws. The values of θ_0 in Eqs. (20b) and (20c) are determined from the kinetic laws (2) and (3), assuming the interface to be moving initially at the steady-state velocity.

Equation (20a) may be solved by applying a Laplace transformation, yielding

$$\Psi(\omega_0 t) = \frac{v}{v_0} = 2e^{B^2\omega_0 t} \text{ erfc } (B\sqrt{\omega_0 t}) - 1. \tag{21}$$

but the nonlinear nature of Eqs. (20b) and (20c) precludes their solution by this method. Instead, numerical solutions to Eqs. (20) may be obtained by replacing the integrals with series approximations, and computing the interface temperature after successive time intervals Δt:

$$\Psi_n (n\Delta\omega_0 t) = 1 - \frac{B}{\sqrt{\pi}} \sqrt{(\Delta\omega_0 t)} \left[2\sqrt{n} + \sum_{m=0}^{n-1} \frac{\Psi_m}{\sqrt{(n-m)}} \right], \tag{22a}$$

$$\theta_n(n\Delta t) = \theta_0 + \frac{A}{\sqrt{\pi}} Pj_0 \sqrt{(\Delta t)} \left[2\sqrt{n} - \frac{1}{\theta_0^2} \sum_{m=0}^{n-1} \frac{\theta_m|\theta_m|}{\sqrt{(n-m)}} \right], \tag{22b}$$

and

$$\theta_n(n\Delta t) = \theta_0 + \frac{A}{\sqrt{\pi}} Pj_0 \sqrt{(\Delta t)} \left[2\sqrt{n} - e^{+\mu_4/|\theta_0|} \sum_{m=0}^{n-1} \frac{\theta_m e^{-\mu_4/|\theta_m|}}{|\theta_m|\sqrt{(n-m)}} \right]. \tag{22c}$$

Figure 4 compares, on an expanded scale, the function $\Psi(\omega_0 t)$ as calculated from (a) the Fourier analysis, Eq. (14), (b) the analytical solution, Eq. (21), of the integral equation, Eq. (20a), and (c) the series approximation, Eq. (22a). The discrepancy between curves a and b is due to the approximation in the integral-equation method that the interface actually attains its steady-state velocity and temperature before the current reversal; the discrepancy between curves b and c represents the error due to approximating the integral by the series. Since these discrepancies are small, it is concluded that the functions $\theta_n(n\Delta t)$ computed from Eqs. (22b) and (22c) will be valid representations of the temperature changes of solid/liquid interfaces with parabolic and exponential kinetics when subjected to a single current reversal. The response of these interfaces to a square-wave current may be approximated by plotting several reversals in succession. The velocities of the interfaces may be computed from the temperatures by use of the kinetic relations, Eqs. (1) through (3); $x(t)$, the position of the interfaces, may be computed as
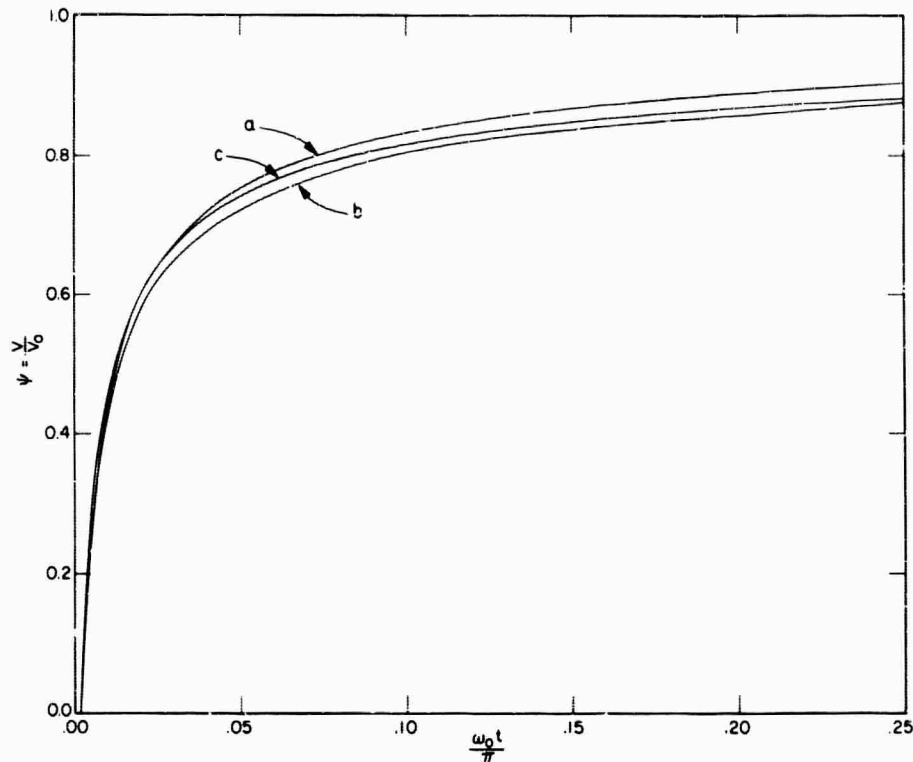
Fig. 4 - Velocity waveform for interface displaying linear kinetics with $B = 10$, calculated by three different methods: (a) Fourier analysis, Eq. (14); (b) analytical solution, Eq. (21), to integral equation; and (c) numerical computation of integral equation

$$\int_0^t v(t') \, dt'.$$

For linear kinetics we obtain

$$x(\omega_0 t) = v_0 \left\{ \frac{2}{B^2} \left[e^{B^2 \omega_0 t} \operatorname{erfc}(B\sqrt{\omega_0 t}) - 1 \right] + \frac{4}{\sqrt{\pi}B} \sqrt{(\omega_0 t)} - \omega_0 t \right\}. \tag{23}$$

while for nonlinear kinetics the integration is performed numerically. The solution for parabolic kinetics shown in Fig. 5 was computed using $\Delta t = 10^{-4}$ sec, $APj_0 = 0.1\sqrt{\pi}$, and $\theta_0 = 0.01$ C°, corresponding to $\mu_2 \approx 3$ cm/sec-°C^2, while Fig. 6 shows the result of a computer solution to Eq. (22c) for a steeply varying exponential kinetic law.

The computed curves indicate that when the solidification kinetics are sufficiently sluggish to distort the waveform of interface motion from a simple sawtooth, the different kinetic laws (Eqs. (1) through (3)) do, in fact, produce significantly different waveforms. Linear kinetics are most rapid and, therefore, the most difficult to detect; while the values of $\mu_1 \approx 0.01$ cm/sec-°C reported for tin by Rigney and Blakely (6) would lead to readily observable kinetic effects in this experiment, these values appear to be too low to be valid estimates (7). If μ_1 is greater than about 1 cm/sec-°C, then it will be extremely difficult to measure the kinetics by means of this experiment. Parabolic or exponential kinetics should lead to more easily observable interface kinetic effects.
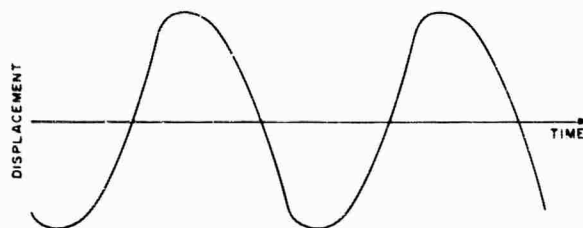
Fig 5 - Interface-displacement waveform
for an interface displaying parabolic ki-
netics with $\mu_2 = 3$ cm/sec-$°C^2$, subjected
to a 40-Hz square wave

Fig. 6 - Interface-displacement waveform
for an interface displaying steeply varying
exponential kinetics, subjected to a 0.6-Hz
square wave. For this interface, $\mu_3 = 1.4 \times 10^{19}$ cm/sec and $\mu_4 = 50 C°$ in Eq. (3).

DISCUSSION

Advantages of Peltier Heating Method

The use of the Peltier effect to introduce heat directly at the solid/liquid interface
has several advantages over methods in which thermal waves must be propagated toward
the interface through the specimen.

The maximum amplitude of the temperature variation occurs directly at the inter-
face and is equal to the kinetic supercooling. Temperature variations diminish rapidly
as one moves away from the interface, Eq. (6), so that frequency-associated convection
in the liquid is reduced to a minimum. The "short circuiting" effect of periodic heat flow
along the container walls, which is a significant problem in the Kramer-Tiller method,
does not arise here since no transport of heat to a temperature sensor is required. The
waveform and amplitude of the heat input at the interface are readily controlled by the
Peltier effect; the use of a square-wave electric current is a convenient way to keep the
Joule heating constant, and the square wave is a useful form for the mathematical analy-
sis of the response of systems with nonlinear kinetics. Finally, direct measurement of
the waveform of interface motion by an electronic method here makes possible the de
termination in a single experiment of the fu :tion relating interface velocity to interface
temperature.

Justification of Approximations

Several effects which might alter the analysis of heat flow as presented in the sec-
tions "Analysis of Heat Flow" and "Expected Waveforms" have been neglected, bu argu-
ments are presented here that the influence of these effects is insignificant.

The flow of part of the periodic heat emission from the interface out through the capillary walls would invalidate the assumption of one-dimensional heat flow and thus affect the motion of the interface; this effect is smaller the larger the diameter of the metal specimen and the higher the fundamental frequency of the square wave. However, increasing the diameter of the specimen would require large increases in both the square-wave amplitude and the higher frequency sine-wave amplitude if the sensitivity of the experiment were to be maintained; moreover, Joule heating would then produce troublesome radial temperature gradients. The magnitude of the electric current can be kept within reasonable limits only if the specimen diameter is not more than a few millimeters. The range of useful square-wave (fundamental) frequencies is limited by the decrease in amplitude of interface motions at high frequencies and the approach of the interface motion to a simple sawtooth at low frequencies. Estimates of reasonable values for kinetic coefficients suggest that useful kinetic data might be obtained at square-wave frequencies of roughly 10 to 20 Hz. At such frequencies the decay distance of the thermal waves propagated into the solid and liquid metal is short [Eq. (6)], and the area over which the container walls are subjected to significant changes in temperature is small. Since the thermal conductivity of the container walls is less than that of the metal by an order of magnitude or more, the frequency-associated heat conduction through the container walls is probably unimportant, even in a 1-mm capillary.

The frequency-associated variations in Joule heating, due to the variation in specimen resistance with interface motion, are much smaller than the amplitude of the Peltier heating square wave induced at the interface. The maximum amplitude of the interface motion (assuming infinite kinetics) will be $X_0 = \pi v_0/\omega_0 = \pi P j_0/\omega_0 \lambda \gamma$. The maximum variation in Joule heating will, therefore, be $\Delta Q_J = I^2(\rho_l - \rho_s) X_0/\pi r^2 = I^2(\rho_l - \rho_s) P j_0/\lambda \gamma \omega_0 r^2$, where ρ_l and ρ_s are the resistivities of the liquid and the solid, and I is the current. Since the Peltier heat peak-to-peak amplitude for a square wave is $\Delta Q_P = 2Pj$, we have $\Delta Q_J/\Delta Q_P = (\rho_l - \rho_s) I^2/2\lambda\gamma\omega_0 r^2 \approx 10^{-6} I^2$ for a 10-Hz square wave in a 1-mm capillary filled with bismuth. Thus, the periodic variation in Joule heating is negligible for currents of a few amperes.

Both the Fourier method and the integral-equation method treated the heat flow from a stationary interface; the heat is considered to emanate from a plane fixed in space, and the change of position of this plane is neglected, although the latent heat resulting from this slight change of position is an essential part of the analysis. It is believed, however, that the error introduced by this approximation is extremely small, as the amplitude of the interface position oscillations is much smaller than the wavelength of the thermal waves emitted by the interface. From Eq. (6a) we can see that the wavelength of thermal waves of angular frequency ω_0 is $L = 2\pi \sqrt{2\alpha/\omega_0}$. The ratio of the maximum amplitude of the interface motion, given in the preceding paragraph, to the thermal wavelength is thus $X_0/L = Pj_0/2\lambda\gamma \sqrt{2\alpha\omega_0}$. Substituting typical values for bismuth of $P = 0.02$ v, $j_0 = 100$ amp/cm^2, $\lambda = 50$ joules/g, $\gamma = 10$ g/cm^3, and $\alpha = 0.05$ cm^2/sec, we have $X_0/L \approx 0.005 \sqrt{\omega_0}$. For waves with fundamental periods of a few seconds or less, the effect of interface motion should thus be very small.

Interpretation of Experimental Results

Thermal-wave experiments are capable of determining only average interface velocity as a function of average interface supercooling. O'Hara, Tarshis, and Tiller (13) have suggested that if some crystallographic facet covers a significant fraction, but not all, of the interface, then a combination of kinetic processes will influence the experiment. The derived kinetic law will then not be indicative of any single kinetic process. O'Hara, et al., also suggest that an experimental finding of linear kinetics may be insufficient to distinguish between a truly continuous growth process and a process involving growth at the edge of layers intersecting the solid/liquid interface.

It is possible that a thermal-wave experiment will not indicate kinetics described by Eq. (2) when growth takes place by a screw-dislocation mechanism. Equation (2) was derived on the assumption that the growth layers emanating from a screw dislocation had assumed their steady-state configuration, so that the spiral growth steps rotated on the surface without changing shape (14). If the direction of interface motion were suddenly reversed, the entire spiral would unwind and then coil up in the opposite sense. During this process of reversal, however, the kinetics would not be described by Eq. (2). Only if the time required for the spiral to approach its steady-state configuration were small compared to the time in which significant changes in interface temperature occur would the system behave as described by Eq. (20b).

Let us consider how some of these uncertainties in the interpretation of experimental results can be resolved. Of primary importance is the measurement of solidification kinetics as a function of crystallographic orientation. Solidification kinetics as described by Eqs. (2) and (3) can take place only if the interface lies on or very close to a low-index crystallographic plane which can grow only by the generation of new layers by screw dislocations or layer nucleation. Planes which are far from low-index planes must always contain an abundance of layer edges and, therefore, would always be expected to show apparent linear kinetics associated with layer spreading. So long as these layer edges are not so close together that they interact with one another, then the apparent linear kinetic coefficient should be directly proportional to the density of layer edges, which is readily related to the crystallographic orientation of the interface. Therefore, in a substance such as bismuth, which appears both macroscopically and microscopically (15) to grow by a layer-spreading mechanism, it is necessary to study a variety of orientations near those which show facets. For example, a screw-dislocation mechanism would be identified if we found parabolic kinetics at and very near the low-index plane, and (apparent) linear kinetics with orientation-dependent coefficient as we moved away from this plane.

Any waveform distortion resulting from transient coiling effects of screw dislocations should depend on the amplitude and frequency of the square wave driving the interface motion; we can conclude that these effects are not important if we obtain consistent results at different amplitudes and frequencies.

CONCLUSIONS

The atomic kinetics of solidification of some substances can be investigated by an analysis of the response of these systems to a square wave of Peltier heat input at the solid/liquid interface. The analysis is possible for nonlinear, as well as linear kinetics. It is found that linear, parabolic, and exponential kinetic laws should yield distinguishable waveforms of interface motion. The consistency of experimental results can be established by investigating crystallization kinetics as a function of crystallographic orientation and of square-wave amplitude and fundamental frequency.

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13 ABSTRACT

Periodic Peltier heating and cooling may be generated at a solid/liquid interface by the passage of an alternating electric current. Melting and freezing will then occur at rates which will be influenced by the kinetic law of molecular attachment relating solidification velocity to interface temperature. The equation describing the interface attachment kinetics may be determined by measuring the response of a solid/liquid interface to square-wave Peltier heating and cooling. The mathematical methods required for extracting the kinetic equation by analysis of the waveform of interface motion show that this technique should give distinguishably different waveforms for linear, parabolic, and exponential kinetics. There are advantages of the method, but precautions must be taken to eliminate possible confusing effects.

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